CONCENTRATIONS OF PCDDs, PCDFs AND PCBs IN SAMPLES OF BUTTER FROM 24 COUNTRIES.

David Santillo[1], Alwyn Fernandes[2], Ruth Stringer[1], Paul Johnston[1], Martin Rose[2] & Shaun White[2]

[1] Greenpeace Research Lab., University of Exeter, Prince of Wales Road, Exeter, EX4 4PS, UK
[2] Central Science Laboratory, Sand Hutton, York YO41 1LZ, UK

Introduction

Residues of PCDD/Fs and PCBs present in butter may indicate the occurrence of these contaminants in pastureland on which cattle graze, and thus provide a useful environmental indicator of fluxes to pastures. These would have principally an atmospheric component although there are also other possible sources of contamination to pastures such as a water-based contribution from irrigation or periodic flooding for cattle grazing on flood plains,[1] and animal feed. Caution must therefore be observed when using this data as an indicator of local environmental contamination. Nevertheless, as previously noted for chlorinated pesticide residues and PCBs[2], the potential for the use of butter as a convenient, widely available and relatively uniform matrix for the determination of spatial trends in distributions of persistent organic pollutants warrants further research. This is especially the case in many countries where research and monitoring programmes are lacking and for which few or no data are therefore available. This study examines the levels of dioxins and PCBs in butter samples taken from 24 different countries around the world (Table 1).

Analytical Methodology

A total of 138 samples of home-produced butter were collected during 1998 from retail outlets (mainly supermarkets) in 24 countries world-wide. Concentrations of organochlorine pesticide residues and total PCBs in 63 samples have been reported previously.[2] A sub-set of 25 butter samples, taken from a wide geographical spread representing 24 countries, was selected for dioxin (PCDD/Fs), *ortho*-substituted and non *ortho*-substituted PCB analysis. Methods used for the extraction and analysis of samples have been previously reported.[3] All measurements were UKAS accredited to the EN 45000 and ISO 25 standards. Additionally, BCR reference materials (CRM 350 for PCBs; RM 533 and RM 534 for the PCDD/Fs) were analysed with each sample batch.

Results and Discussion

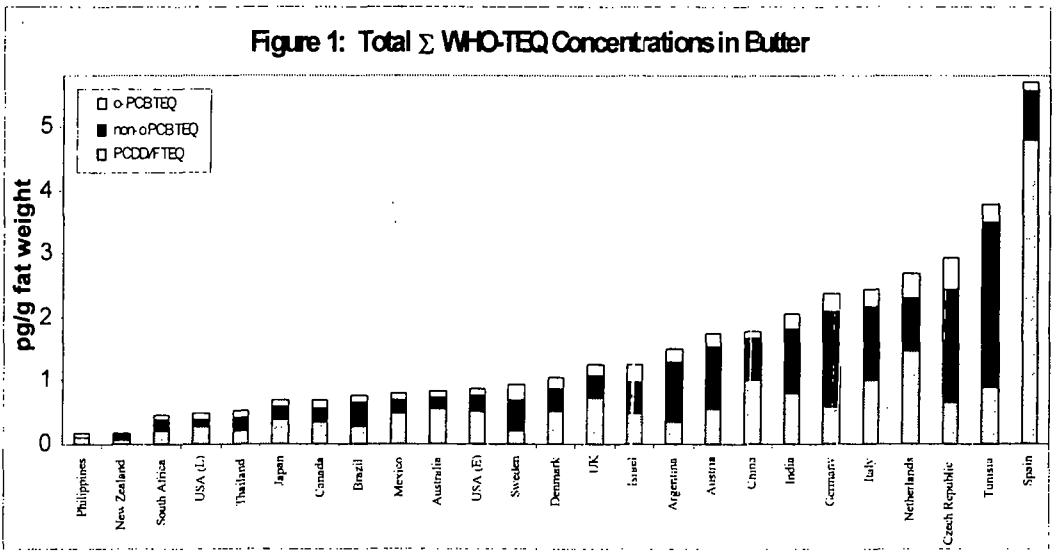
Toxic equivalents, both I-TEQ and WHO-TEQ (based on WHO-TEFs for mammals) and Σ ICES 7 PCB data for all samples, as well as literature data are reported on a fat weight basis in Table 1.

Distribution of TEQ values

PCDD/F and PCB concentrations were compared with similar data on butter reported in the literature,[4-7] and a good general agreement was found. The non-*ortho* PCB contribution was large for samples from Tunisia, the Czech Republic, Germany and Argentina, and relatively small for other samples such as Spain, Australia, Mexico and the Philippines. In the case of the Czech

Republic, Tunisia and Germany the contribution to the ΣWHO-TEQ from non-*ortho* PCBs was almost three times higher than that from PCDD/Fs.

Two types of contributory pattern were seen; those samples with a higher PCDD/F contribution to the TEQ (West of Europe, North America, the Far East and South Africa) and those with a higher PCB concentration (Central Europe, South America and India).



Individual Congener Profiles

PCDD/F congener profiles for many of the samples included in the current study shared characteristics with those reported for butters collected from Germany between 1993 and 1996[4]. The profiles reported for butters from Germany and the Netherlands collected in 1998[5-6] were less similar, possibly because of contamination by citrus pulp which was likely to have contributed to the PCDD/F burden of these samples (Table 2). For example, concentrations of 2,3,7,8-TCDD and 1,2,3,7,8-PCDD were notably higher in the 1998 German and Dutch samples than in those included in the current study. Conversely, concentrations for HpCDD and OCDD for the 1998 German and Dutch samples were at the lower end of the range determined for the samples in the current study. Although mean TEQs for the eight butters from Spain[7] were in a similar range as those recorded in the current study, congener profiles show much higher concentrations of OCDD and OCDF in the Spanish butters (Table 2).

In this study, relatively high concentrations of HpCDD were recorded in butters from Mexico, USA and Israel, and of OCDD for Mexico, USA, Israel, China, India and Australia. Only 4 PCDD/F congeners were found at levels above limits of detection in the butter sample from New Zealand. The highest dioxin concentration recorded was for 2,3,4,7,8-PeCDF in the sample from Spain (7.7 pg/g). This value however is greatly elevated compared to the next highest value for the same congener, of 0.94 pg/g detected in the Chinese butter sample. This elevated level of 2,3,4,7,8-PeCDF is accompanied by relatively high values for $T_4 - H_6$ Cl PCDF congeners, and the I-TEQ profile of this sample shows similarities to that of a blood sample from a Yusho patient[8].

This may indicate a similar type of source, *i.e* a PCB mixture, although the ΣICES 7 PCB concentration was not particularly elevated for this sample.

Table 2: Selected PCDD/F & PCB concentrations compared to literature values (pg/g).

Congener	2,3,7,8-TCDD	1,2,3,7,8-PCDD	2,3,4,7,8-PeCDF	1,2,3,4,6,7,8-HpCDD	OCDD	OCDF	PCB 77	PCB 126
This study	< 0.02 - 0.43	< 0.02 - 0.43	< 0.01 - 7.73	0.09-3.04	0.19 - 4.07	0.02-0.31	0.22 -10.8	0.1 - 25
[4]Germany (1993-1996)	nd-0.26	nd-0.48	0.18-2.47	0.22-2.12	0.75-4.76	nd-0.67		
[5]Germany (1998)	0.36-0.62	0.37-0.52	0.54 - 0.70	0.41-0.79	0.59-0.84	0.28-0.50		
[6]Nether-lands (1998)	0.9	0.64	0.98	0.42	0.45	0.16		
[7]Spain (1998)	nd-1.11	nd-1.08	nd-2.06	0.58-3.09	1.35-26.6	nd-3.18	0.03 - 1.83	nd - 0.62

Of the non-*ortho* PCBs, the highest levels were observed for PCB 126, with Tunisia, the Czech Republic, Germany and Italy showing the highest values. This congener has the highest WHO-TEF value of any PCB and the concentrations observed in this study make it the largest contributor to the total ΣWHO-TEQ. India, China and the Philippines showed high absolute concentrations of PCB 77 relative to PCB 126.

Conclusions

Concentrations of PCDD/Fs in butter samples from 24 countries fell within a similar range to the previously reported data for European butters, with the exception of a single sample from Spain. This sample showed the highest I-TEQ and ΣWHO-TEQ of all samples, and displayed a PCDD/F profile which showed similarities to that previously observed for a PCB contaminated sample.[8]

The inclusion of dioxin-like PCBs to give a total ΣWHO-TEQ had a marked effect on the TEQ levels for some countries notably Tunisia, the Czech Republic, Germany and Argentina. The Europe/North Africa region shows the highest mean concentrations of all the contaminants measured when compared to the other regions included in this study. The levels of contaminants observed for the butter samples do not correlate with economic indicators such as GDP or Industrialisation data for the corresponding countries.

Interpretation in terms of more specific regional variations are somewhat limited by the inclusion of only a single sample for each country (and two for the USA). It is not possible, for example, to state that the concentrations determined represent an average level for each of the countries included in the study. Substantial regional variation in contamination may clearly be expected within countries, dependent on the geography of the butter's source. Nevertheless, the data from the current study, along with those previously reported for PCBs and pesticide residues in butters from the same sample set[2], indicate the utility of butter as a convenient integrative matrix for the monitoring of spatial distributions of persistent organic pollutants. In this context, it is hoped that these studies can make a significant contribution to the development of global networks for POP monitoring, an activity of central importance to the developing UNEP POPs Convention.

References

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Table 1: Summary of TEQ (pg/g fat) and PCB (ng/g fat) concentrations in butter.

Identity	WHO-TEQ				I-TEQ	PCBs
	PCDD/F	non-o PCB	o-PCB	Σ TEQ	PCDD/F	Σ ICES 7
Philippines	0.11	0.01	0.06	0.18	0.11	0.45
New Zealand	0.06	0.07	0.06	0.19	0.05	0.32
South Africa	0.21	0.17	0.08	0.46	0.17	0.94
USA (G. Lakes)	0.27	0.13	0.08	0.48	0.22	0.99
Thailand	0.22	0.21	0.11	0.54	0.19	1.31
Japan	0.40	0.20	0.09	0.69	0.34	0.60
Canada	0.35	0.21	0.14	0.70	0.28	1.44
Brazil	0.28	0.39	0.10	0.77	0.23	1.10
Mexico	0.50	0.21	0.09	0.80	0.43	1.01
Australia	0.56	0.19	0.09	0.84	0.44	0.72
USA (East Coast)	0.54	0.23	0.11	0.88	0.45	1.62
Sweden	0.20	0.51	0.22	0.93	0.18	4.22
Denmark	0.52	0.37	0.16	1.05	0.44	3.44
UK	0.75	0.35	0.15	1.25	0.57	2.66
Israel	0.50	0.49	0.26	1.25	0.43	3.71
Argentina	0.36	0.92	0.21	1.49	0.31	2.38
Austria	0.55	0.99	0.22	1.76	0.45	7.17
China	1.01	0.65	0.13	1.79	0.90	1.85
India	0.79	1.01	0.25	2.05	0.69	3.59
Germany	0.58	1.51	0.28	2.37	0.51	10
Italy	1.03	1.14	0.26	2.43	0.87	7.58
Netherlands	1.46	0.85	0.39	2.70	1.25	7.46
Czech Republic	0.66	1.80	0.46	2.92	0.59	27
Tunisia	0.91	2.58	0.28	3.77	0.75	14
Spain	4.80	0.74	0.17	5.71	4.61	4.33
Mean - this study	0.70	0.64	0.18	1.52	0.62	4.42
Median - this study	0.52	0.39	0.15	1.05	0.44	2.38
[5]Germany 1998 – Range, 4 samples	1.18 – 1.67				1.00 - 1.41	
[6]Netherlands 1998 - Single sample	2.29				1.97	
[7]Spain 1998 – Mean of 8 brands					1.09	
[4]Germany '93-'96, Mean, 222 samples	0.74				0.64	